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(54) **Pigments of improved dispersibility in thermoplastic resins.**

(57) A pigment composition of improved dispersibility in thermoplastic resins and concentrates of the pigment composition in thermoplastic resin are provided. The pigment composition is comprised of an inorganic pigment such as titanium dioxide having an organophosphate ester treating agent deposited thereon.

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Background of the Invention**1. Field of the Invention**

5 The present invention relates to compositions of matter characterized by their improved dispersibility in thermoplastic resins. More particularly, the present invention relates to chemically treated inorganic pigments suitable for use in thermoplastic resins. Most particularly, the present invention relates to titanium dioxide pigments treated with an organophosphate ester treating agent.

10 2. Description of the Prior Art

The use of inorganic pigments such as, for example, pigmentary titanium dioxide, as UV light stabilizers, colorants, opacifiers and the like in various thermoplastic resins is known. It also is known, however, that due to the hydrophilic nature of such inorganic pigments and to the hydrophobic nature of the 15 thermoplastic resins, the compatibility and thus the dispersibility of such pigments in such resins, particularly at high pigment loadings, leaves much to be desired.

It further is known that the compatibility and thus the dispersibility of inorganic pigments in thermoplastic resins can be significantly improved through chemical surface treatment of the pigments. For example, in U.S. Pat. No. 4,209,430 it is disclosed to treat inorganic pigments such as titanium dioxide pigment with 20 phosphorylated polyenes, i.e., aliphatic polyunsaturated compounds of at least ten carbon atoms to which a phosphoryl group has been added to the olefinic unsaturation thereof. The pigments thus treated are described as not only possessing improved pigment properties but also improved uniformity of dispersion and a reduced tendency to yellow in those thermoplastic polyolefins to which the treated pigments may be added.

25 Further examples of methods or treatments for reducing the tendency of inorganic pigments, and particularly titanium dioxide, to yellow in various polymeric compositions are those disclosed in U.S. Pat. Nos. 4,357,170 and 4,377,417. According to these patents, the application to pigmentary titanium dioxide of an additive system comprised of either the combination of an organophosphate/alkanolamine addition product and a polyol or the organophosphate/alkanolamine addition product alone results in a reduction of 30 the tendency of titanium dioxide pigment to yellow in polymeric compositions. The organophosphate materials utilized to produce the addition product include those organophosphate materials disclosed in U.S. Patent No. 3,380,927. These materials comprise orthophosphate or polyphosphate coesters of, conjointly, an aliphatic alcohol containing 6 to 16 carbon atoms and a nonionic adduct of ethylene oxide and a reactive hydrogen containing organic compound. The organic compound employed to form the adduct include 35 alkylated phenols, aliphatic alcohols containing 6 to 25 carbon atoms, aliphatic monocarboxylic acids and the like. Neither U.S. Patent No. 4,357,170 nor U.S. Pat. No. 4,377,417 mentions any benefit to be afforded by such treatment relevant to the dispersibility of the thus treated pigment when employed in a polymeric composition.

40 A still further example of the treatment of inorganic fillers or pigments with organophosphate esters is found in U.S. Pat. No. 4,183,843. This patent teaches the surface treatment of inorganic fillers or pigments, including titanium dioxide, with polar phosphate ester surfactants containing both acid and polar ether groups. The thus treated fillers or pigments, when combined with a sprayable, curable polyester resin results in filler or pigment/polyester dispersions of reduced viscosities. Although the exact nature or structure of the treating materials is not definitively identified, materials such as Triton QS-44, a product of 45 Rohn and Haas, listed as an exemplary coating material is known to comprise the composition, octyl-phenoxyethoxyethylphosphate.

None of the foregoing patents suggest either the treated organic pigments or the polymeric concentrates produced therefrom which are the subject of this application.

50 5. Summary of the Invention

In accordance with the present invention, there are provided inorganic pigments characterized by possessing an improved dispersibility in thermoplastic resins. The improved inorganic pigments, preferably titanium dioxide pigments, have deposited thereon at least one organophosphate ester treating agent 55 corresponding to the general formula $[RO(R'O)_x]_3PO$. In this formula, R represents a monovalent lower alkyl radical containing from about 1 to about 6 carbon atoms, R' is a divalent hydrocarbon radical selected from the group consisting of ethylene and propylene radicals and x is a number ranging from about 1 to about 15.

The present invention further relates to pigmented polymeric concentrates comprising as a continuous phase a thermoplastic resin and as a disperse phase the above described organophosphate ester treated inorganic pigments.

5 **Detailed Description of the Invention**

The inorganic pigments which can be subjected to treatment with the hereinafter described organophosphate ester treating agents to provide the improved inorganic pigments of the present invention include any of the white or colored, opacifying or nonopacifying particulate inorganic pigments (or mineral pigments) known and employed in the surface coatings (e.g., paint) and plastics industries. For purposes of this present description, the term inorganic pigments is employed broadly to define materials which are particulate by nature and nonvolatile in use and typically are most usually referred to as inerts, fillers, extenders, reinforcing pigments and the like.

10 Representative but non-limiting examples of inorganic pigments which can be treated as herein described to provide the improved inorganic pigments of this invention include white opacifying pigments such as titanium dioxide, basic carbonate white lead, basic sulfate white lead, basic silicate white lead, zinc sulfide, zinc oxide, lithophane (a composite pigment of zinc sulfide and barium sulfate) antimony oxide and the like, white extender pigments such as calcium carbonate, calcium sulfate, china and kaolin clays, mica, diatomaceous earth and colored pigments such as iron oxide, lead oxide, cadmium sulfide, cadmium 20 selenide, lead chromate, zinc chromate, nickel titanate, chromium oxide and the like. Of all the inorganic pigments useful in producing the improved inorganic pigments of the present invention, a most preferred pigment is that of pigmentary titanium dioxide.

15 In general, the preferred titanium dioxide pigment for use in preparing an improved pigment of this invention can be of either the anatase or rutile crystalline structure or combination thereof. This pigment may be produced by way of various known commercial processes which are familiar to those of skill in this art but which processes do not form any part of the present invention. Thus, this particular pigment can be one produced by either the well known sulfate process or the well known vapor phase oxidation process. The former process, i.e., the sulfate process, typically involves the steps of leaching a titaniferous ore with sulfuric acid to produce a titanium sulfate solution, hydrolysis of the titanium sulfate to form a titanium 25 dioxide precipitate and calcination of this precipitate in the presence of suitable additives to develop the desired crystalline structure in the final calcined titanium dioxide product. In the latter process, i.e., the vapor phase oxidation process, a titanium halide such as titanium tetrachloride is oxidized in the vapor phase at elevated temperatures to produce what is commonly referred to as raw titanium dioxide. This raw pyrogenic titanium dioxide product then is recovered, subjected to milling and classification operations and, 30 following treatment to deposit various hydrous metal oxide coatings upon the pigment, subjected to a final treatment to provide a pigment of the desired particle size.

35 Typically, the final milling step will comprise the use of fluid energy milling techniques. These techniques involve conveying the pigment through a milling apparatus such as the fluid energy mills disclosed in U.S. Patent Nos. 2,032,827 and 2,219,011 using one or more gaseous streams produced by jets of a milling fluid such as air or steam to effect collision between individual pigment particles and thus a reduction in size of such particles. Various additive materials may be incorporated into the pigment during the fluid energy milling either to improve the milling of the pigment as disclosed in U.S. Patent No. 3,531,310 or to enhance particular chemical, physical and optical properties of the resultant milled pigment as disclosed in U.S. Patent No. 4,752,340. Representative, but non-limiting, examples of such additive 40 materials include polyols such as glycerol, pentaerythritol, trimethylolethane, trimethylolpropane and the like, fatty acids such as oleic acid, stearic acid and the like, trialkanolamines such as triethanolamine and the like and amine salts such as triethanolamine malonate, triisopropanolamine succinate and the like.

45 The amounts of the above disclosed additive materials which can be employed may vary broadly. Such broad variance depends upon both the particular additive material employed and the particular purpose for which it is added. Thus, for example, additive materials employed as aids to the milling of the titanium dioxide pigment will be utilized in amounts ranging from about 0.05 to about 5.0 weight percent based on the weight of the pigment. The amounts of the additive materials employed to modify any one or more of the chemical, physical or optical properties of the pigment typically will range from about 0.01 to about 3.0 weight percent based on the weight of the pigment.

50 Like the additive materials disclosed above, the organophosphate ester treating agents employed to provide the improved titanium dioxide pigment and the other inorganic pigments of this invention also can be readily deposited onto this pigment during the fluid energy milling thereof. However, other convenient methods for treating the titanium dioxide and the other inorganic pigments disclosed herein with the

organophosphate ester treating agent can be used. Such other methods include, for example, applying the treating agent to the pigments by spraying or otherwise mixing the treating agent with the dry pigments. Thus the treating agent can be applied to the pigments by addition of the treating agent to the pigments through the intensifier bar of a V-blender or by spraying the treating agent into a screw conveyor or paddle 5 mixer containing the pigments.

As disclosed hereinabove, the organophosphate ester treating agents useful in providing the inorganic pigments of improved thermoplastic resin dispersibility include those compounds corresponding to the general formula, $[RO(R'O)_x]_3PO$. In this formula, R is defined as being a monovalent alkyl radical containing from 1 to 6 carbon atoms, preferably from 2 to 4 carbon atoms and most preferably 4 carbon atoms, R' is 10 defined as being a divalent hydrocarbon radical selected from the group consisting of ethylene and propylene radicals, preferably an ethylene radical and x is defined as a number ranging from about 1 to about 15, preferably from about 1 to about 5 and most preferably 1. The monovalent alkyl radical, R, in this formula, can be either a straight-chain or branched-chain alkyl radical. Representative examples of such radicals include methyl, ethyl, n-propyl, isobutyl, n-pentyl, isopentyl, n-hexyl radicals and the like. Non- 15 limiting examples of organophosphate ester treating agents useful in preparing the improved inorganic pigments of the present invention include tri(methoxyethyl) phosphate, tri(butoxyethyl) phosphate, tri(isobutoxyethyl) phosphate, tri(hexoxyethyl) phosphate, tri(ethoxypolyethoxyethyl) phosphate, tri(ethoxypolypropoxypropyl) phosphate, and the like.

The amount of organophosphate esters (or triesters) employed to treat the inorganic pigments 20 described hereinabove, and particularly titanium dioxide pigment, will be an amount sufficient to provide a treated pigment exhibiting a dispersibility in thermoplastic resins greater than that of the pigment prior to treatment. Broadly, the amount of the organophosphate ester (or triester) treating agent employed will be an amount ranging from about 0.1 to about 5 weight percent based upon the weight of the pigment, preferably an amount ranging from about 0.3 to about 1.2 weight percent.

25 The resulting organophosphate ester treated inorganic pigments can be employed to readily and uniformly pigment a wide variety of thermoplastic resins. These include such well known classes of thermoplastic resins as polyolefin resins, acrylic resins, polyester resins, polyamide resins, epoxy resins, phenolic resins, poly(vinylaromatic) resins, poly(vinylhalide) resins, polycarbonate resins, polyurethane resins, and the like. Representative, but non-limiting, examples of these various classes of thermoplastic 30 resins include: polyolefin resins such as polyethylene, polypropylene, and the like; acrylic resins such as poly(acrylic acid), poly(methacrylic acid), poly(methylacrylate), poly(methylmethacrylate), and the like; polyester resins such as poly(ethylene terephthalate), poly(butylene terephthalate) and the like; polyamide resins such as nylon-6 and nylon-6,6, and the like; epoxy resins such as poly(epichlorohydrin/bisphenol A) and the like and esters thereof such as those prepared by the esterification of poly- 35 (epichlorohydrin/bisphenol A) with a fatty acid, resin acid, tall oil acid or mixtures thereof; phenolic resins such as those derived from the reaction of formaldehyde with phenol, resorcinol, cresol, p-phenylphenol, and the like; poly(vinylaromatic) resins such as polystyrene and copolymers thereof such as poly(styrene-acrylonitrile), poly(styrene-butadiene-acrylonitrile), and the like; poly(vinylhalide) resins, such as poly-(vinylchloride), poly(vinylchloride/vinylidene chloride) and the like; polycarbonate resins such as those 40 attained either by the phosgenation of dihydroxy aliphatic or aromatic monomers such as ethylene glycol, propylene glycol, bisphenol A (i.e., 4,4'-isopropylidene diphenol), and the like or by the base catalyzed transesterification of bisphenol A with diphenyl carbonate to produce bisphenol A polycarbonate; and polyurethane resins obtained by the reaction of di- or polyfunctional hydroxy compounds such as glycols or hydroxyl terminated polyesters and polyethers with di- or polyfunctional diisocyanates.

45 The amounts of the organophosphate ester treated inorganic pigments of this invention which can be added directly to the above described thermoplastic resins can vary widely depending upon the intended end use for these resins. Thus, thin films sometimes will require very high pigment levels while thick parts may only require a very small percentage. Accordingly, the amount of the treated pigment employed can range from as little as about 1 weight percent to as much as about 80 weight percent based upon the 50 weight of the thermoplastic resin.

In yet a further embodiment of the present invention, the organophosphate ester treated inorganic pigments of the present invention have exhibited particular utility in the preparation of dispersed pigment concentrates. Broadly, these dispersed pigment concentrates will comprise a continuous phase constituting a thermoplastic resin and a disperse phase constituting the organophosphate ester treated inorganic 55 pigments of this invention. The continuous phase may comprise any of the thermoplastic resins hereinbefore described, including the polyolefin resins, acrylic resins, polyester resins, polyamide resins, epoxy resins, phenolic resins, poly(vinylaromatic) resins, poly(vinylhalide) resins, polycarbonate resins, polyurethane resins, and the like.

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In preparing the dispersed pigment concentrates of the present invention, the amount of pigment incorporated into the thermoplastic resin continuous phase can vary widely. In general, this amount will vary depending upon the level of pigmentation desired or required in the final or finished end product employing these dispersed pigment concentrates as pigmenting vehicles, and the effectiveness of the processing equipment utilized to reduce, dilute or dissolve the dispersed pigment concentrates in the thermoplastic resins used to produce the final or finished end products. Broadly, the dispersed pigment concentrates of this invention may contain weight ratios of the treated inorganic pigment to the thermoplastic resin in which it is dispersed ranging from about 0.5:1 to about 5:1. Within such range, the treated inorganic pigment of the present invention can be easily and uniformly dispersed or distributed throughout the thermoplastic resin employed as the continuous phase of the dispersed pigment concentrate produced.

Processes and process equipment useful in the preparation of the above described dispersed pigment concentrates are known and do not form any part of this aspect of this invention. Such known processes generally involve mixing and/or blending techniques utilizing equipment capable of handling high plastic viscosity materials. Illustrative of equipment typically employed in mixing and/or blending processes include various kneader type dispersers, such as the Banbury mixer, single and multi-role mills, and the like. A more detailed description of such mixing and/or blending processes and the equipment which may be employed therein can be found in Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Ed., Vol. 15, pages 592-596.

The invention is further described and illustrated by the following examples. These examples represent specific embodiments of the invention and are not to be construed as limitations thereon.

Example 1

A rutile titanium dioxide product of the Kerr-McGee Corporation of Oklahoma City, Oklahoma marketed under the trade designation CR-834 and having a median particle size of about 0.33 microns was treated in accordance with the present invention. That is, the particulate titanium dioxide was dry treated with tri(butoxyethyl) phosphate as a fine mist or spray at a concentration of about 1% by weight of pigment. Specifically, the titanium dioxide and tri(butoxyethyl) phosphate were mixed in a v-blender in which the tri(butoxyethyl) phosphate was added through the intensifier bar.

The dispersibility of the treated titanium dioxide as compared to untreated titanium dioxide was then determined. That is, the mixing bowl of a Brabender Plasticorder was loaded with 36.50 g of a polystyrene resin marketed by the Dow Chemical Company under the trade designation STYRON® #615, 0.31 g of zinc stearate as a lubricant and 109.50 g of the above described treated titanium dioxide. The bowl temperature was set at 40°C and the blade speed at 150 rpm. The torque and temperature were then recorded vs time. The procedure was repeated using untreated titanium dioxide in order to compare the dispersibility of the treated titanium dioxide with untreated titanium dioxide. The results of these tests are set forth in Table 1 below.

TABLE 1

Pigment Tested	Torque, Metergrams	Temperature, °C
Untreated	1616	182
Tri(butoxyethyl) Phosphate treated	1340	173

The lower torque and temperature of the treated titanium dioxide as compared to untreated titanium dioxide indicates that the treated titanium dioxide has a greater dispersibility than the untreated titanium dioxide.

Example 2

The procedure of Example 1 was repeated except that instead of being compared with untreated titanium dioxide, the dispersibility of treated titanium dioxide of the present invention is compared with Kerr-McGee Company CR-834 rutile titanium dioxide treated with 1% by weight of pigment of a phosphorylated polyene treating agent of the type disclosed in U.S. Patent No. 4,209,430 issued June 24, 1980 which is incorporated herein by reference, i.e., Sylvakote K pigment dispersing agent (Sylvacote K is a trademark of Sylvakim Corp.). The results of this comparison are set forth in Table 2 below.

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TABLE 2

Pigment Tested	Torque, Metergrams	Temperature, °C
Sylvakote K treated	1450	171
Tri(butoxyethyl) Phosphate treated	1370	166

5 From Table 2 it can be seen that the treated titanium dioxide pigment of the present invention exhibits a
 10 lower torque and temperature, and therefore, a greater dispersibility than the same titanium dioxide pigment
 treated with a phosphorylated polyolefin treating agent.

Example 3

15 The procedure of Example 1 was repeated except that the titanium dioxide pigment treated in
 accordance with the present invention is compared to the same titanium dioxide pigment treated (1% by
 weight of pigment) with various of the coating materials disclosed in U.S. Patent No. 4,183,843 issued
 January 15, 1980 which is incorporated herein by reference. The results of these tests are set forth in Table
 3 below.

20 TABLE 3

Pigment Tested	Torque, Metergrams	Temperature, °C
Triton QS-44 treated	1455	181
Wayfos D-10N treated	1432	179
Wayfos M-60 treated	1433	179
Wayfos M-100 treated	1411	178
Tri(butoxyethyl) Phosphate treated	1320	173

30 The data of Table 3 demonstrates the lower torque and temperature, and therefore, the greater
 dispersibility of the treated pigment of the present invention as compared with pigment treated with polar
 phosphate esters.

35 Example 4

The titanium dioxide described in Example 1 was treated (1% by weight of pigment) with tri-
 40 (butoxyethyl) phosphate in a Jet'O mill manufactured by Fluid Energy Processing and Equipment Company.
 The dispersibilities of the treated titanium dioxide and untreated titanium dioxide were determined as
 described in Example 1. The results are set forth in Table 4 below.

TABLE 4

Pigment Tested	Torque, Metergrams	Temperature, °C
Untreated	1599	187
Tri(butoxyethyl) Phosphate treated	1278	173

50 Example 5

55 Samples of treated and untreated titanium dioxide pigment (Kerr-McGee Co. CR-834) were tested for
 dispersibility. A Banbury mixer was charged with 47.6 kg (105 pounds) of Dow Chemical Company
 STYRON No. 615 Polystyrene, 2.3 kg (5 pounds) of conventional processing aids and 90.7 kg (200 pounds)
 of the titanium dioxide sample. The batch temperature during mixing was determined as was the melt flow
 rate of the mixed material when extruded. The treated and untreated titanium dioxide pigments tested and
 the results of the tests are set forth in Table 5 below.

TABLE 5

Pigment Tested	Batch Temp. °C (°F)	Melt Flow Rate, g/10 minutes
Untreated	159 (319)	27.1
Untreated	163 (325)	35.7
Sylvacote K treated	149 (301)	57.0
Tri(butoxyethyl) Phosphate treated	146 (294)	65.6

From Table 5 it can be seen that the titanium dioxide treated in accordance with the present invention has the lowest batch mixing temperature and the highest melt flow rate indicating the greatest dispersibility.

Claims

1. A pigment composition comprising an inorganic pigment having deposited thereon at least about 0.1 percent by weight based upon the weight of said pigment of an organophosphate ester of the general formula:
[RO(R'O)_x]₃PO wherein R is a monovalent alkyl radical of 1 to 6 carbon atoms, R' is ethylene or propylene, and x is a number of from 1 to 15.
2. A composition according to claim 1 wherein the inorganic pigment comprises titanium dioxide.
3. A composition according to claim 1 or 2 wherein the amount of organophosphate ester deposited the inorganic pigment is 0.1 to 5 percent by weight.
4. A composition according to any one of claims 1 to 3 wherein R in the said general formula is alkyl of 2 to 4 carbon atoms, R' is ethylene, and x is a number from 1 to 5.
5. A composition according to claim 4 wherein R is alkyl of 4 carbon atoms and x is 1.
6. A dispersed inorganic pigment concentrate comprising, as a continuous phase, a thermoplastic resin and, as a disperse phase, a pigment composition as claimed in any one of claims 1 to 5.
7. A dispersed inorganic pigment concentrate according to claim 6 wherein the said thermoplastic resin is a thermoplastic homo- or copolymer resin.
8. A dispersed inorganic pigment concentrate according to claim 7, wherein the said thermoplastic homo- or copolymer resin is a polyolefin, polyvinyl, polyacrylic, phenolic, alkyd, epoxy, nylon, polyurethane, phenoxy, polycarbonate or polyester resin.
9. A dispersed inorganic pigment concentrate according to claim 7 wherein the said thermoplastic homo- or copolymer resin is a polyolefin or a polyvinyl resin.
10. A dispersed inorganic pigment concentrate according to any of claims 6 to 9 wherein the weight ratio of the treated pigment to the thermoplastic resin in said concentrate is from 0.5:1 to 5:1.